

PUB-NO: EP000508746A1

DOCUMENT-IDENTIFIER: EP 508746 A1

TITLE: Internally oxidised Ag-Sn-In alloy electrical contact materials and manufacturing method thereof.

PUBN-DATE: October 14, 1992

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APPL-NO: EP92303107

APPL-DATE: April 8, 1992

PRIORITY-DATA: JP16408991A (April 9, 1991)

INT-CL (IPC): C22C032/00, H01H001/02

EUR-CL (EPC): C22C032/00 ; H01H001/02

US-CL-CURRENT: 200/262

ABSTRACT:

Electrical contact materials are made of internally oxidized Ag-Sn Solid-Solution type alloys of 5-20 weight % Sn, added by a trace amount of more than 0.1 weight % to less than 1 weight % of In. Such addition of In is effective to have Sn oxides precipitated not too finely in said Ag-Sn alloys, whereby their electrical characteristics, especially electrical contact resistances thereof are improved, and subsequently their temperature rising is held low.



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(11) Publication number : **0 508 746 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number : **92303107.4**

(51) Int. Cl.⁵ : **H01H 1/02, C22C 32/00**

(22) Date of filing : **08.04.92**

(30) Priority : **09.04.91 JP 164089/91**

(43) Date of publication of application :
14.10.92 Bulletin 92/42

(84) Designated Contracting States :
DE FR GB

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(54) **Internally oxidised Ag-Sn-In alloy electrical contact materials and manufacturing method thereof.**

(57) Electrical contact materials are made of internally oxidized Ag-Sn Solid-Solution type alloys of 5-20 weight % Sn, added by a trace amount of more than 0.1 weight % to less than 1 weight % of In. Such addition of In is effective to have Sn oxides precipitated not too finely in said Ag-Sn alloys, whereby their electrical characteristics, especially electrical contact resistances thereof are improved, and subsequently their temperature rising is held low.

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Background of the Invention

This invention relates to those electrical contact materials which are widely used with electrical apparatuses such as switches, breakers, contactors, and so on. It shall be noted that the electrical contact materials made in accordance with this invention are those made from Ag-Sn-In alloys which have been prepared by a melting method and internally oxidized, and differ from those prepared by mixing and sintering powdered Ag and oxidized and powdered Sn and In by a powder metallurgical method.

As an electrical contact material for the above-mentioned use, Ag-Cd oxides alloys are known. However, since Cd is harmful to health, they have been replaced by Ag-Sn oxides alloys without the employment of Cd. Such Ag-Sn oxides alloys are most extensively employed today as contact materials. Since it is considerably difficult to completely internally oxidize Sn of Ag-Sn alloys when Sn is contained therein at a rate more than 5 weight %, In is added to the alloys as an auxiliary solute metal element.

In this end, In has to be added as much as more than 2%, although In oxides have a low refractoriness and comparatively weak in hardness. Therefore, the present inventors have pursued to internally oxidize, without the addition of In, solid-solution type alloys contained with more than 5 weight % of Sn. They were successful in the internal oxidation of such alloys which was conducted in an oxygen atmosphere of more than 10 atm, as disclosed in U.S. Patent No. 5, 078, 810.

Although the solid-solution type alloys which contain more than 5% of Sn only and without any other solute metal, and which have been successfully internally oxidized by the present inventors at described above, are provided with well-oriented alloy structures, Sn oxides precipitated in the alloys are however too fine. As the result, their conductivity becomes somewhat low, and contact resistance becomes unstable and high sometimes. This invention is to solve such problems.

Brief Summary of the Invention

The present invention provides electrical contact materials made of solid-solution type alloys consisting of 5-20 weight % of Sn, more than 0.1 weight % to less than 1 weight % of In, and the balance of Ag, and which has been internally oxidized. The present invention further provides a method for making electrical contact materials, which comprises activating solid-solution type alloy consisting of 5-20 weight % of Sn, more than 0.1 weight % to less than 1 weight % of In, and the balance of Ag, by preheating, followed by internally oxidizing the alloys by heating them in an oxygen atmosphere of more than 10 atmospheres to 200 atmospheres and at a temperature of 750 to 500°C to that the alloys are kept in solid phase and do not liquify.

In this invention, Ag-Sn of 5-20 weight % alloys which have been prepared by melting procedures at distinguished from powder metallurgy procedures, are internally oxidized with the addition to the alloys of a trace amount of In. The above-mentioned lower limit percentage of Sn is, when Sn is oxidized, to afford to the alloys such refractoriness with which they can work at electrical contacts. And, the upper limit of Sn is not to make the alloys too brittle.

Although internally oxidized Ag-Sn-In alloy electrical contact materials made in accordance with this invention are same to conventional ones with respect to their constituent metal elements, their In amounts are remarkably different.

To wit, in this invention, the In amount is more than 0.1 weight % to less than 1 weight %. Such trace amount of In is not workable as an auxiliary element for assisting or accelerating the oxidation of Sn, but unexpectedly workable to make oxidized precipitates of Sn coarse. This is a novel discovery the present inventors have made through repeated experiments.

The effects brought by In as mentioned above, could improve conductivities of Ag-Sn of 5-20 weight % solid-solution type alloys which have been internally oxidized, and could contribute remarkably to make their contact resistances stable and low.

In this invention, one or more of iron family elements, that is, Fe, Ni, and Co may be added to the alloys at an amount of 0.001 to 1 weight % in total so as to regulate alloy structures.

Examples

- (1) Ag-Sn 6%-In 0.8%
- (2) Ag-Sn 9.5%-In 0.9%
- (3) Ag-Sn 9.5%-In 0.1%-Ni 0.2%
- (4) Ag-Sn 6%

The above alloy (1), (2), and (3) were prepared by melting the above mentioned constituents and cast to ingots of 120mm in diameter and 400mm in length. The above alloy (4) which belongs to a prior art, was likewise

made to an ingot, for its comparison with the alloys (1), (2), and (3) of this invention. Each alloy ingot was hot-pressed to a square bar of 30mm in thickness and 50mm in width. The bar was cut to a length of 500mm, and its upper and lower surfaces were shaved off in 3mm each to obtain a bar of 24mm in thickness, 50mm in width, and 500mm in length.

5 To the shaved lower surface, pure silver of 2.5mm was hot-bonded. The bar was then rolled to a sheet having a thickness of 1.2mm, and punched out to obtain disk-shaped contacts of 6mm in diameter and 1.2mm in thickness. After they had been preheated in a furnace at 500°C, they were internally oxidized by heating them to 700°C in an oxygen atmosphere of 25 atm for 48 hours.

10 Microscopic observation of them, the alloys (1), (2), (3), and (4) which were vertically cut out showed that the Sn elements had been completely internal oxidized, not producing any subscale in their outer surface areas.

Oxidized precipitates of Sn of the contacts made from the alloy (4) as described above were extremely fine and were distributed evenly throughout the Ag matrices, irrespectively of their Ag grain boundaries. Although structures of the alloys (1), (2), and (3) were also fine and even as if they were made powder-metallurgically, their oxidized precipitates of Sn were not so too extremely fine as in the alloy (4).

15 The aforementioned preheating of the alloys in advance of the internal oxidation is for activating them so that oxygen could penetrate smoothly into the alloys when they are subjected to baking for the internal oxidation.

In this invention in which the internal oxidation of Ag-Sn of 5-20% alloys is made by adding thereto a trace amount of In and by heating them in an oxygen atmosphere of more than 10 atm, it is desireable to make a heating temperature comparatively low when an oxygen pressure is high, and vice versa. To wit, when the oxygen atmosphere is comparatively low above 10 atm, the heating temperature will be held comparatively high

20 within the range of about 500-750°C, while when the oxygen atmosphere is made comparatively high above 10 atm, the heating temperature will be held comparatively low within the above-mentioned range.

It is desireable also to internally oxidize the alloys in this invention by keeping them under a solid phase without involving any liquidous phase thereof, because if the alloys become liquidous, oxidized solute elements 25 will be transferred to surface areas of the alloys, producing subscales thereof about said areas.

Although when the heating temperature is selected to the lowest among the aforementioned range, the oxygen atmosphere could be made as higher as possible so far as alloys would not present a liquidous phase, about 200 atm is maximum therefor, because such is practical in carrying out this invention economically and technically advantageously at an industrial scale.

30 Conductivities (IACS%) and hardness (HRS) of the above contacts obtained by the internal oxidation of the alloys (1), (2), (3), and (4) are respectively as shown in the following Table 1.

Table 1

	Conductivity (IACS%)	Hardness (HRS)
(1)	69	82
(2)	57	90
(3)	55	91
(4)	72	78

45 Their initial contact resistances by ASTM-50 testing machines under the following conditions are as given in the following Table 2. Their temperature rising (higher than a room temperature) at terminals connected to them after testing for 1,000 switching cycles are also shown in the Table 2.

Conditions for initial contact resistance:

50 Contact force 400g
Current DC6V, 1A

Conditions for temperature rising tests:

Load AC200V, 50A
Reactor pf=0.23

55 Frequency 60 cycles/minute

Table 2

	Initial contact resistance ($\text{m}\Omega$)	Temperature Rising ($^{\circ}\text{C}$)
5	(1)	0.5
	(2)	0.7
10	(3)	0.7
	(4)	0.8
		30
		35
		35
		36

As seen in the above test results, the electrical contact materials made in accordance with this invention
 15 are afforded with such conductivities which are satisfactory well within the range of practically employable values. And, their electrical characteristics, especially their initial contact resistances are considerably improved, and their temperature rising in use is lowered subsequently.

The present invention has been described above purely by way of examples and modifications can be made
 20 within the invention.

20

Claims

1. Electrical contact materials made of solid-solution type alloys consisting of 5 to 20 weight % of Sn, more than 0.1 weight % to less than 1 weight % of In, and the balance of Ag, and which have been internally oxidized.
 25
2. The electrical contact materials as claimed in Claim 1, further comprising 0.001 to 1 weight % in total of one or more of Fe, Co, or Ni.
3. The electrical contact materials as claimed in Claims 1 or 2, which have been internally oxidized in an oxygen atmosphere of more than 10 atm and under a condition which has not made the alloys liquidous.
 30
4. The electrical contact materials as claimed in Claims 1, 2, or 3, which have been internally oxidized, after having been preheated to have the alloys activated, in an oxygen atmosphere of more than 10 atm to 200 atm and at a temperature of 750 to 500°C.
 35
5. The electrical contact materials as claimed in Claim 1, which is added by one or more elements of 0.001 to 1 weight % in total selected from Fe, Co, and Ni of the iron family.
6. A method for making electrical contact materials, which comprises activating by preheating alloys of the solid-solution type consisting of 5 to 20 weight % of Sn, more than 0.1 weight % to less than 1 weight % of In, and the balance of Ag, subsequently followed by the internal oxidation of the alloys by heating them in an oxygen atmosphere of more than 10 atm to 200 atm and at a temperature of 750 to 500°C so that the alloys are kept in a solid phase not involving the liquidity of the alloys.
 40
7. The method as claimed in Claim 6, the alloys further comprising 0.001 weight % to 1 weight % in total of one or more of Fe, Co, or Ni.
 45
8. The method as claimed in Claim 6, in which the alloys are added by one or more elements of 0.001 weight % to 1 weight % in total which are selected from Fe, Co, and Ni of the iron family.
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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 3107

DOCUMENTS CONSIDERED TO BE RELEVANT						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.S)			
Y	FR-A-2 395 582 (CHUGAI DENKI KOGYO) * claims 1-7 *	1-8	H01H1/02 C22C32/00			
Y	DE-A-2 908 923 (CHUGAI DENKI KOGYO) * abstract; claim 1; example 2 *	1-8				
A	FR-A-2 394 880 (CHUGAI DENKI KOGYO) * page 3, line 5 - line 11 *	1,3,5,6				
A	EP-A-0 219 924 (CHUGAI DENKI KOGYO) * abstract *	1,6				
			TECHNICAL FIELDS SEARCHED (Int. CL.S)			
			H01H C22C			
<p>The present search report has been drawn up for all claims.</p> <table border="1"> <tr> <td>Place of search BERLIN</td> <td>Date of completion of the search 08 JULY 1992</td> <td>Examiner NIELSEN K.G.</td> </tr> </table>				Place of search BERLIN	Date of completion of the search 08 JULY 1992	Examiner NIELSEN K.G.
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